METHODS FOR DETERMINING AROMATICS AND BENZENE IN REFORMULATED GASOLINES

R. E. Pauls and G. J. Weight
Amoco Research Center
150 West Warrenville Road
Naperville, IL 60563-8460

ABSTRACT

The recently passed Clean Air Act places a number of restrictions upon the composition of gasolines marketed in ozone and CO nonattainment areas. These restrictions include upper limits on the total aromatic and benzene contents of the reformulated gasolines. As a result, reliable, routine analytical methods will be required to certify the aromatic and benzene content of gasolines.

Although a number of different approaches are available for the determination of these properties, many are unsuited for routine analysis, especially in smaller refineries. This presentation will review chromatographic methods currently available for these measurements. In addition, the accuracy and precision of several of these methods for the determination of the aromatic and benzene content of reformulated fuels will be discussed.

INTRODUCTION

The effects of motor vehicle exhaust and running losses upon urban air quality has prompted the regulation of the composition of automotive fuels. The recently passed Clean Air Act places restrictions in a number of instances upon the maximum aromatic and benzene content of gasolines. Concerns over benzene arise because it is a known carcinogen and it along with 1,3-butadiene, formaldehyde and acetaldehyde are the major toxic compounds found in vehicle exhaust. To meet the requirements of these regulations, the oil industry will need reliable analytical methods. Among the requirements of these methods are acceptable precision, freedom from bias, and freedom from interferences due to oxygenates.

BENZENE METHODS

A number of different chromatographic methods are currently available for the determination of benzene in gasoline. For comparison purposes, these can be subdivided into 4 classes:

1) Single column gas chromatographic methods
2) Column switching gas chromatographic methods
3) Multi-column PIONA methods
4) Liquid chromatographic methods

Single column methods may employ either long capillary columns containing non-polar stationary phases or, alternately, columns containing highly polar stationary phases such as TCEP. The former are commonly referred to as single column PONA methods and typically employ 100 m columns with internal diameters of 0.25 mm and a film thickness of 0.5 μm methyl silicone stationary phase (1). These columns rely on their high inherent separation power to resolve benzene from other closely boiling components such as 1-methylcyclopentene. Separation of benzene from other hydrocarbons on TCEP columns (2) is based upon the significantly greater retention of aromatic compounds relative to non-aromatics of similar boiling point on polar stationary phases. Both these single column methods suffer limitations due to long analysis times and possible co-elution of

other components.

An example of a column switching approach to determine benzene is ASTM D 3606
(3). The method employs a non-polar column to perform an initial separation
based upon boiling point followed by a polar column to separate benzene and
toluene from other, closely boiling hydrocarbons. Heavier components are
backflushed to waste. Figure 1 illustrates a typical separation of gasoline by D
3606. Note the rapid analysis time and good resolution of benzene and toluene
from other components. MTBE is not an interference in this method. There is
some partial overlap with methanol and ethanol but resolution is sufficient to
permit accurate quantitative measurement (4).

Multi-column PIONA methods provide a distribution of paraffins, iso paraffins,
olefins, naphthenes and aromatics by carbon number (5). As benzene is the only
C_6 aromatic, benzene values can be obtained directly from PIONA methods.
However, when only benzene values are of interest, this is a costly and time
consuming approach.

Benzene may also be rapidly determined by liquid chromatography employing C_{18}
reversed-phase columns and water/acetonitrile mobile phases with refractive index
detection (6). Figure 2 contains a plot comparing the results obtained on
approximately 100 samples with D 3606 and the LC method. The slope and intercept
are close to unity and zero, respectively indicating little relative or fixed
bias between the two methods. In our laboratory, we prefer to employ D 3606
because it has demonstrated better precision than the LC method. Table 1
contains a comparison of the repeatability obtained in our laboratory of these
two methods for a gasoline sample:

TOTAL AROMATICS

The accurate measurement of total aromatics is considerably more difficult to
achieve than the determination of benzene. The ideal requirements for a total
aromatics method would include that it be simple, inexpensive, accurate, precise
and free from oxygenate interferences. The same 4 basic approaches discussed
above for measuring benzene can also be employed to measure total aromatics. In
addition, the traditional FIA method, ASTM D 1319 (7) is widely employed for this
purpose. This method is based upon displacement chromatography with fluorescent
dyes to indicate boundary regions between saturates, olefins and aromatics.
Although widely employed for a number of years, this method suffers from a number
of deficiencies including poor precision, operator dependency, long analysis
times, and difficulties with automation. Additional chromatographic methods for
measuring total aromatics include supercritical fluid chromatography (SFC) and an
EPA proposed method that employs GC/MS. Recently SFC with flame ionization
detection has been employed to measure aromatics in diesel and jet fuels (8). A
similar approach may be suitable for gasoline. GC/MS approaches have not been
widely employed because of their additional complexity, difficulties with
calibration, and the high cost of such methods.

The two different single column approaches described above for benzene are also
suitable for total aromatics. The PONA approach requires that all aromatic peaks
be assigned and the total summed. In contrast, an advantage of using a highly
polar stationary phase such as Carbowax derivatives or TCEP for measuring total
aromatics is that the aromatics tend to be isolated into the end of the
chromatogram. These can be summed as a group. Except for the early eluting
peaks, benzene and toluene, it is not necessary to identify each individual
aromatic peak. Figure 3 illustrates the separation of a gasoline on a DB-Wax
megabore capillary column. Although LC methods have been employed to monitor
hydrocarbon types in fuels, this approach has in general been limited by detector

response problems (9).

Most of our recent efforts in this area have been devoted toward developing a rugged, routine column switching method for measuring total aromatics. Such a method could be more suitable for refinery applications than previously discussed approaches. ASTM Method D 4420 was employed as the basis for our work. It was modified in 4 ways: an internal standard was added, a flame ionization detector was employed, a different column set was employed than that specified in the D 4420 method, and the analysis was performed in two steps to minimize interferences from non-aromatics. The first two changes were made to enhance the quantitative aspects of the analysis. The column set was modified to incorporate the same columns as used by ASTM D 4815, a method to determine oxygenates in gasoline. These columns are a 1/16 inch TCEP packed column and a methyl silicone megabore column. This change was implemented to enhance resolution and speed.

Figure 4 illustrates the valve configuration employed in this method. We perform this analysis in two steps. Initially the sample is injected through injector B onto the TCEP column. Non-aromatics compounds, out to approximately n-decane, elute prior to benzene and are vented to waste through a thermal conductivity detector. Six seconds prior to the elution of benzene, the valve is actuated and components not eluted from the TCEP column are backflushed onto a methyl silicone megabore column. Once C_8 aromatics have eluted from the megabore column, the valve is switched to its original position and C_9+ aromatics are backflushed to the detector. All measurements of aromatics are made with the flame ionization detector. Figure 5 contains a chromatogram resulting from this analysis. Only the benzene and toluene values are used from this first analysis.

The analysis is repeated a second time with the valve switching time increased to a time 6 seconds prior to the elution of ethyl benzene from the TCEP column. This step is performed to reduce the possibility of interference due to high boiling non-aromatics. These compounds would normally be found in the C_9+ fraction. Figure 6 contains a chromatogram resulting from this analysis. Note the differences in the peaks of the C_9+ fractions in Figures 5 and 6. Table 2 contains a comparison of the C_9+ results from the first and second analyses. T90 values are also provided. As expected, lower values were obtained for C_9+ aromatics with the longer cut time. This is due to the exclusion of some higher boiling non-aromatics. The greatest discrepancy was observed for the samples with the highest endpoint. The C_8 and C_9+ values from the second run are combined with the benzene and toluene values obtained on the first run to obtain total aromatics. Comparisons of this method with alternate approaches such as PIONA indicate a high correlation between total aromatics for the two methods. Common oxygenates including MTBE, methanol and ethanol do not interfere with the aromatic peaks in the modified D 4420.

SUMMARY

A number of different chromatographic approaches are available for the measurement of benzene and total aromatics. In our laboratory, we prefer to employ D 3606 to determine benzene because of its high precision and fast analysis times. A wide range of alternative methods may be employed to measure total aromatics. Our current work has focused upon modification of ASTM D 4420 to provide a rugged, reliable method using proven column switching methodology.

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Table 1. Comparison of the Precision of ASTM D 3606 and an LC Method for the Determination of Benzene

	D 3606[a]	LC[b]
Mean (wt%)	0.73	0.72
Standard Deviation (wt%)	0.007	0.022
Relative Standard Deviation (%)	0.96	3.1
Repeatability (wt%)	0.019	0.061
Number of measurements	24	50

Table 2. Effect of Cut Time on C_8 and C_9+ Aromatics Measurements by Modified D 4420

Sample	Vol% C_8 Aromatics		Vol% C_9+ Aromatics		T90(°F)
	Cut Time 1	Cut Time 2	Cut Time 1	Cut Time 2	
A	11.6	11.3	16.4	15.5	330
B	4.25	4.12	15.0	11.9	357
C	6.32	6.22	5.89	5.19	280
D	5.75	5.70	22.0	19.7	350

Detector Response

Benzene

Internal Standard

Toluene

Time (min)

5   10
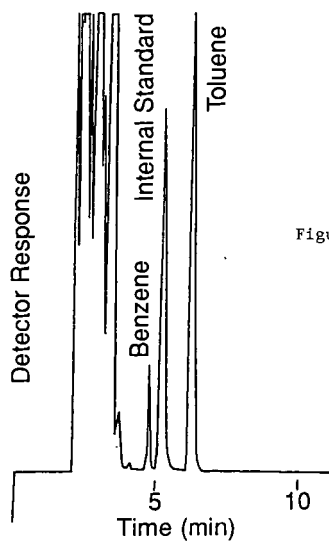
Figure 1   Chromatogram of a gasoline by ASTM Method D 3606

Wt % Benzene, LC

Wt % Benzene, D 3606

Slope = 1.01
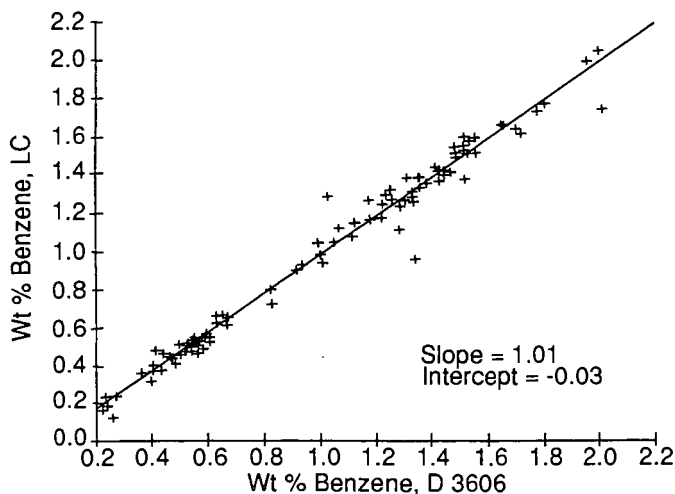Intercept = -0.03

Figure 2   Comparison between D 3606 and Liquid Chromatography for the determination of benzene in gasoline blending stocks.

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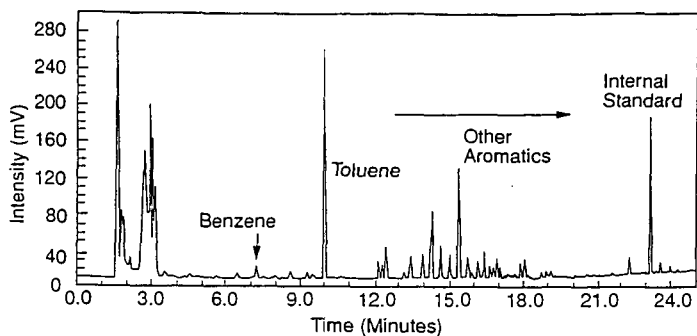Figure 3 Chromatogram of a gasoline on a DB-Wax capillary column. Gasoline diluted with benzene-free carbon disulfide.
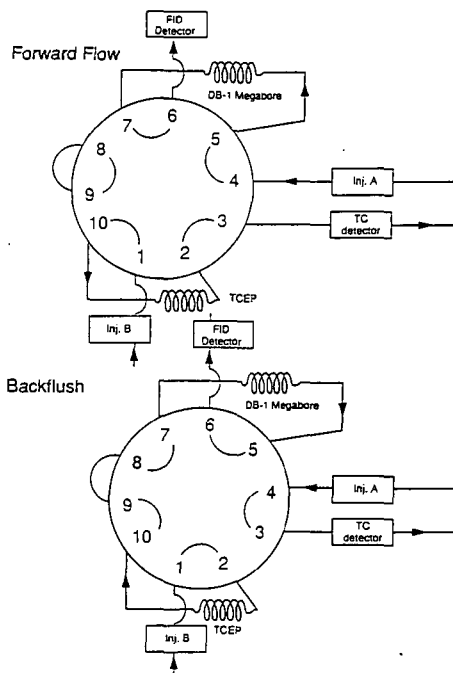

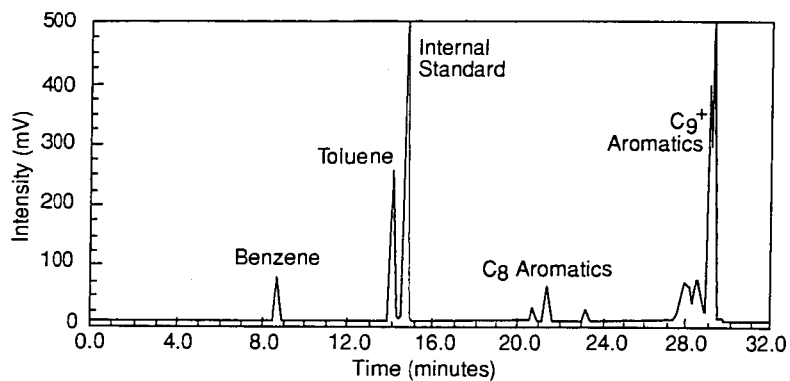Figure 4 Valve configuration for modified D 4420
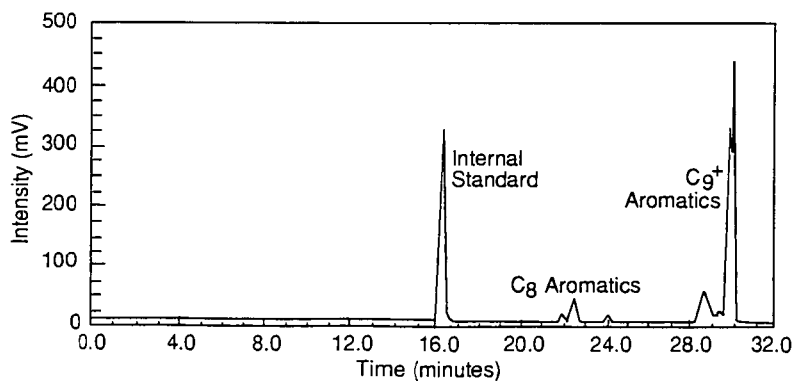
Figure 5   Chromatogram of gasoline with first valve cut time.

Figure 6   Chromatogram of gasoline with second valve cut time.

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